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Composite synth tic r sin panes

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Abstract

A transparent composite synthetic resin pane, especially for the glazing of vehicles, comprises; a) a transparent synthetic resin substrate pane, preferably of approximately constant thickness; b) at least one transparent synthetic resin film, optionally provided on the surface remote from the substrate pane with a weather- and/or scratch-resistant synthetic resin layer; and c) at least one transparent adhesive resin layer between the substrate pane and the synthetic resin film and more firmly adherent to the synthetic resin film than to the substrate pane whereby the adhesive resin layer is detachable together with the synthetic resin film from the substrate pane. The invention also provides a detachable synthetic resin wear film for use in the production of composite panes as described above.

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(54) Composite synthetic resin panes

(57) A transparent composite synthetic resin pane, especially for the glazing of vehicles, comprises:

a) a transparent synthetic resin substrate pane, preferably of approximately constant thickness;

b) at least one transparent synthetic resin film, optionally provided on the surface remote from the substrate pane with a weather- and/or scratch-resistant synthetic resin layer; and

c) at least one transparent adhesive resin layer between the substrate pane and the synthetic resin film and more firmly adherent to the synthetic resin film than to the substrate pane whereby the adhesive resin layer is detachable together with the synthetic resin film from the substrate pane. The invention also provides a detachable synthetic resin wear film for use in the production of composite panes as described above.

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SPECIFICATION

Composite synthetic resin panes

This invention relates to composite synthetic resin panes and their use as glazing material especially for vehicles.

Synthetic resin panes and composite synthetic resin panes are already used as glazing materials. The scratch sensitivity of these panes is generally higher than that of mineral glass panes and is therefore considered to be a disadvantage. Scratch-resistant coatings based on silicone compounds or applied by vapour deposition of silicon oxides give a temporary protection, but the useful life of the pane, especially under weathering, remains restricted by the still limited scratch-resistance or by the adhesive strength of the scratch-resistant layer.

It is known to protect synthetic resin panes from damage of the sensitive surface during transport and processing by the application of a temporary protective covering of paper or synthetic resin film. These protective coverings are removed prior to the use of the object equipped with synthetic resin pane. According to British Patent Specification No. 582,253 acrylic glass panes may be provided with a protective covering of polyvinyl alcohol applied in the form of an aqueous solution and then dried. Although the covering is transparent and colourless, it is not water-proof and not of an optical quality sufficient to permit undistorted vision through the pane. Consequently, these coverings are also, in principle, removed after the fitting of the pane. In Japanese Patent Specification No. 7614554 are described protective films of PVC, containing plasticiser, which have an adhesive resin layer on one side of the films and a silicone-rubber layer with enhanced abrasion-resistance on the other. Such films are also suitable only for temporary protection of the surface of a synthetic resin pane and, in any case, are removed before use. protective sheet of mineral glass which can be porotective sheet of mineral glass which can be applied by means of a soft, elastic adhesive resin intermediate layer is known from Swiss Patent Specification No. 456,127. Although this provides a scratch-resistance corresponding to that of mineral glass, the breaking strength of the protective mineral glass sheet is too low and visibility is gradually impaired during use as cracks and flaws appear in the protective sheet. Since the sheet cannot be detached, the entire pane then has to be replaced.

The coating of a mineral glass pane with a synthetic resin film is known from U.S. Patent Specification No. 3,681,179. The film may be provided with a metallic coating to reflect the sun's radiation. Also known is the application of tough clear synthetic resin sheets as shatter protection in case of breakage of the mineral glass pane.

None of these methods provide synthetic resin panes which can be left in their plac of use for an unlimited length of time without having to be removed and replaced due to damage to their surfaces.

It is an object of the present invention to provide transparent synthetic resin panes for glazing purposes, especially for the glazing of vehicles, which, even under the action of surface-damaging influences, do not need to be replaced owing to impaired visibility.

Whereas the hitherto known protective measures served exclusively either to protect synthetic resin panes against damage for the duration of an increased danger to their surfaces, namely transport and installation, by providing a coating to be detached before use or to make the useful surfaces of the panes as resistant as possible to damaging effects, the present invention is based upon a different concept whereby the useful surfaces, the gradual damage of which appears to be unavoidable, are designed to be replaceable by new surfaces as soon as visibility is impaired by scratches or any other surface damage.

According to one aspect of the present invention we therefore provide a transparent composite synthetic resin pane comprising:

a) a transparent synthetic resin substrate pane, preferably with the two surfaces of greatest surface area approximately parallel and advantageously at least 1 mm in thickness;

b) at least one transparent synthetic resin film, optionally provided on the surface remote from the substrate pane with a weather-resistant transparent synthetic resin layer and/or a scratch-resistant, preferably silicon-based, transparent synthetic resin layer, and advantageously being such that the scratch-resistance of the wear surface of the synthetic resin film is no lower than that of the substrate pane; and

c) at least one transparent adhesive resin layer between the substrate pane and the synthetic resin film and more firmly adherent to the synthetic resin film than to the substrate pane whereby the adhesive resin layer is detachable together with the synthetic resin film from the substrate pane. Preferably the adhesive resin layer is to strongly bonded to the synthetic resin wear film that it is irremovable without damaging the latter.

According to a further aspect of the present invention we also provide a detachable synthetic resin wear film for use in the production of composite panes as described above and comprising:

a) at least one transparent synthetic resin film, optionally provided on the surface remote from the substrate pane with a weather-resistant transparent synthetic resin layer and/or a scratch-resistant, preferably silicon-based, transparent synthetic resin layer, and advantageously being such that the scratch-resistance of the wear surface of the synthetic resin film is no lower than that of the substrate pane;

b) at least one transparent adhesive resin layer firmly adherent to the said transparent synthetic resin protective film; and

c) if desired, a removable protective coating

adherent to the surface of the adhesive resin layer remote from the transparent synthetic resin protective film.

When surface-damaging influences act only on one side of the pane, as with picture frames or instrument glazing, the synthetic resin serving as replaceable surface may be attached to only one side of the substrate pane, but preferably a synthetic resin film is attached to both sides of the substrate pane. As a rule, replacement of the scratched film by a new film will involve a substantially smaller outlay of material and labour than the replacement of the entire pane.

Any synthetic resin pane in itself suitable as glazing material may be used as a substrate pane. It may be planar or cylindrically curved. To provide optically undistorted visibility, the substrate pane should have parallel surfaces, that is it should be of uniform thickness. The surface dimensions, of the substrate may range from a few square centimetres to several square metres. The thickness depends on the strength requirements and will generally lie between 1 and 8 mm. The substrate pane may be a composite pane of several synthetic resin panes or of synthetic resin and mineral glass panes, with at least one outer surface being of synthetic resin.

The preferred material for the substrate pane according to the present invention is acrylic glass. [The term "acrylic glass" is used herein to designate homopolymers of methyl methylacrylate and copolymers involving a predominant proportion of methyl methacrylate and subordinate quantities of other monomers copolymerisable therewith as well as copolymers of methyl methacrylate with a predominant quantity of acrylonitrile.] The acrylic glass panes may be manufactureed by polymerisation between glass panes and advantageously have a molecular weight of the polymer of at least one million. The substrate pane may also be manufactured by the extrusion and subsequent calendering of thermoplastic acrylic glass; in this case, polymers with a molecular weight of from 100,000 to 300,000 are suitable.

The substrate pane may also consist of other hard synthetic resins with a glass temperature advantageously above 300 K, preferably above 350 K. Such synthetic resins as, for example, polystyrene, polyvinyl chloride and especially polycarbonate are suitable in this context.

To ensure that the synthetic resin film need not be replaced too frequently, there are advantageously used according to the present invention films whose scratch-resistance is not smaller than that of the substrate pane. One method for determining the scratch-resistance numerically which may be applied to the substrate pane and to the film involves measuring the light scattering after the action of a specific wear load; the method is laid down in detail in ASTM D 1044. With increasing destruction of the loaded surface by scratches an increasing proportion of the light incident at the surface is scattered. The proportion of the light scattered relative to the incident light, expressed as a percentage, therefore represents a useful measure of the scratch-resistance; the greater the scratch-resistance, the lower the percentage value.

In general, the proportion of light scattered at the substrate and film surfaces should not be greater than about 30% after a wear load of 100 revolutions of the friction wheels (Taber Abraser) used in accordance with ASTM D 1044 and loaded with 5 Newtons each. Preferably, synthetic resin films whose scratch-resistance clearly exceeds that of the substrate pane and gives a value of at most about 5% with the specified test method are used. Especially preferred are synthetic resin films with a special scratch-resistance coating and a light-scatter value of less than about 1%.

A high scratch-resistance can be imparted to synthetic resin films by many known methods. Examples include the provision of silicate layers (according to U.K. Patent Specification No. 1,365,630, French Patent Specification No. 1099087 or German Offenlegungsschrift 1,521,294) by the vapour deposition of silicon oxides, or with the additional use of aluminium oxide (according to German Auselegeschrift 1,204,084), or with simultaneous glow discharge as described in German Offenlegungsschrift 20 00848. According to U.S. Patent Specification No. 2,771,378 silicate layers can be produced by the hydrolysis of silicon tetrachloride. Scratch-resistant coatings based on silicon compounds are obtained from polysiloxanes (U.S. Patent Specification No. 3,451,838), from ethyl orthosilicate (U.S. Patent Specification No. 2,408,540), from methyl trialkyloxysilane (U.S. Patent Specification No. 3,650,808), from a combination of colloidal silicon dioxide and a silanol part condensate (German Patent Specification No. 2,446,279) and also with biaxially stretched polymethyl methacrylate (U.S. Patent Specification No. 3,720,699). Highly cross-linked organic polymers likewise increase the scratch resistance, for example layers of aminoplast resins (as described in U.S. Patent Specification Nos. 2,481,809 and 3,420,733 and German Offenlegungsschrift 2,317,874) in combination with the urethane resins described in German Offenlegungsschrift 2,611,783 or coatings of multiply unsaturated monomers such as allyl methacrylate (German Auslegeschrift 1,181,407, German Patent Specification No. 1,014,741 and U.S. Patent Specification No. 2,423,583), ethylene glycol dimethacrylate (U.S. Patent Specification No. 2,413,973 and German Patent Specification No. 1,014,741), ethylene - bis - allyl carbonate (French Patent Specification No. 1,460,725) or tri - and - tetra - acrylates or - methacrylates of polyols hardened with ultra-violet radiation (German Offenlegungsschrift 2,455,715). The thickness of the scratch-resistant coatings may, for example, be from 1 to 20 microns. Synthetic resin films with suitable coatings in use on motor vehicles may even have a life of one or more years before they are so

damaged that they need to be replaced.

The detachable film should effect the visibility through the composite synthetic resin pane as little as possible. Consequently, the use of calendered, optically undistorted film is preferred. In order reliably to prevent damage to the synthetic resin pane, the synthetic resin film should have a thickness clearly exceeding the conventional depth of scratches. Films of 20 to 150 microns, preferably 30 to 80 microns, in thickness are especially suitable.

The material of the film is selected so that a minimum of weathering, yellowing or other disturbing effects of ageing will occur during the lifetime limited by the scratch sensitivity. Water-soluble films or films which swell strongly in water, such as polyvinyl alcohol or cellulose films, are particularly unsuitable for use in exposed outdoor locations. If a useful life of one year or more under free weathering is to be provided, such as, for example, for vehicle glazing, then highly weather-resistant materials, preferably polymethyl methacrylate, are especially suitable. Biaxially stretched films are generally to be preferred. The film or at least one layer thereof may contain ultra-violet absorbers (for example those known *per se*), light protection agents and, if desired, a pigment for tinting, although colourless films are preferred.

Under certain circumstances it is sufficient if a film which is weather-resistant only to a limited degree, for example a polycarbonate film, is covered with a thin layer of highly weather-resistant plastic such as, for example, polymethyl methyacrylate. Properties which otherwise do not coincide in a film material, such as, for example, the high toughness of a basic film of polyester or polycarbonate and the weather resistance of the covering layer, may then be simultaneously utilized in such composite films.

The adhesive used to attach the film to the substrate pane should adhere more firmly to the film than to the substrate pane. Otherwise, the adhesive remaining on the pane when the film is detached has to be removed carefully before the application of a replacement film. Adhesive resin layers adhering to the substrate surface with a pull-off force of 10 to 200 N/cm are very suitable. The desired good adhesion between the film and the adhesive is generally obtained if the adhesive layer is applied to the film, for example in a manner known *per se*.

Advantageously, adhesives are used which contain neither constituents which age under the influences of light and weathering nor plasticisers which would penetrate into the substrate pane. Especially advantageous are pemanently elastic adhesives such as, for example, those based on acrylate polymers and which are known *per se*. The adhesive may be applied to the film as aqeuous dispersions or solutions in organic solvents to give a dry layer thickness of for example 2—50 microns. Known adh sives with glass temperature below 250 K are suitable. The adhesive layer should, like the film itself, be optically undistorted, completely transparent and homogeneous and preferably colourless in order not to impair visibility and, furthermore, should either become brittle or yellow nor visibly age during the useful life of the film so adhered.

The adhesives preferable for use according to the invention are polymers or copolymers composed predominantly of alkyl esters of acrylic acid, and advantageously having 4 to 12 carbon atoms in the alkyl radical. As a rule, these esters form at least 80% by weight of the polymer. The lower alkyl esters of acrylic acid with 1 to 4 carbon atoms in the alkyl radical as well as the alkyl esters of methacrylic acid, styrene, vinyl chloride, vinylidene chloride or vinyl acetate may participate in smaller quantities in the composition of the copolymers. Preferably, comonomers with polar groups participate in the composition of the copolymers in subordinate quantities, as a rule not more than 20% by weight; these include acrylic or methacrylic acid, itaconic acid, maleic acid anhydride, hydroxyalkyl esters and aminoalkyl esters of acrylic or methacrylic acid, amides of these acids, especially N-alkyl-substituted acrylamides or methacrylamides such as N-octyl-acrylamide or N-tert-butyl-acrylamide or -methacrylamide. Small quantities, preferably not more than 1% by weight, of cross-linking monomers with two or more polymerisable double bonds are advantageous. Also, mixtures of various polymers are frequently used as adhesive resins, for example mixtures of the above-described acrylate polymers and acrylate copolymers with polyvinyl alkylethers or oxyethylated polyvinyl alcohol. Typical pressure-sensitive adhesive resins suitable for use in the present invention are described in, for example, U.S. Patent Specification Nos. 3,558,574 and 3,617,362.

Before application to substrate pane (e.g. in a known manner), the adhesive layer of the film may be covered by a protective coating of paper or plastic film which is removed before the application. To facilitate an exactly fitting application of the film, it is convenient to use a protective coating of several parts, so that the still covered part of the film can be positioned accurately on the substrate, while the exposed part of the adhesive layer is applied to the relevant portion of the substrate pane. A protective coating consisting of three parallel strips is especially appropriate, whereby the middle strip, which overlaps the two outer strips, is removed before the film is applied. Thus, the film may first be stuck along the exposed middle strip while being accurately held in position by means of the remaining strips.

With such an adhesive system as that described in U.S. Specification No. 3,681,179 the permanently elastic adhesive layer is protected by a water-soluble dry coating. The substrate pane is moistened, the film is laid thereon and the intermediate water layer in which the protective coating dissolves is displaced from the centre outwardly. In this way, the protective film may be applied especially simply in a bubble-free and

crease-free manner.

A film especially suitable for the purpose of the present invention may consist of the following layers:

1. Scratch-resistant silicone synthetic resin layer (preferably about 10 microns).

2. Weather-resistant layer of polymethyl methacrylate (0.2 to 30 microns).

3. Polycarbonate basic film (30 to 80 microns).

4. Adhesive base on polyethyl hexylacrylate (2 to 30 microns).

5. Water-soluble protective coating of a vinyl ether/maleic acid copolymer. The figures in brackets above are the layer thicknesses.

The transparent synthetic resin panes according to the invention are used according to the invention as glazing members. In contrast to the known manufacture of glazing members from synthetic resin panes with a temporarily applied protective film which is removed after the fitting of the pane and before the actual use thereof as glazing material, according to the invention the film-coated composite synthetic resin pane is employed as the actual glazing member. Window glazing and furniture glazing are important areas of application for the composite panes of the invention. A preferred embodiment of the present invention is the equipping of vehicles, especially motor vehicles, with a glazing of the composite panes according to the invention. The saving in weight is of great importance not only with aircraft, but increasingly so with motor vehicles as well. The use of synthetic resin panes in motor vehicles has hitherto been rather restricted due to their unavoidable scratch-sensitivity. The present invention permits the use of synthetic resin panes in vehicles without a regular replacement of the fitted pane becoming necessary. The panes according to the invention offer special advantages in vehicles where they are exposed to a relatively small degree to surface-damaging influences. Thus, the panes of the present invention are particularly suitable for use when fitted to lie approximately parallel to the direction of travel of the vehicle.

CLAIMS

1. A transparent composite synthetic resin pane comprising:

a) a transparent synthetic resin substrate pane;

b) at least one transparent synthetic resin protective film; and

c) at least one transparent adhesive resin layer between the substrate pane and the synthetic resin protective film and more firmly adherent to the synthetic resin film than to the substrate pane whereby the adhesive resin layer is detachable together with the synthetic resin protective film from the substrate pane.

2. A composite pane as claimed in claim 1 wherein the two surfaces of greatest surface area of the said substrate pane are approximately parallel.

3. A composite pane as claimed in either of claims 1 or 2 wherein the said substrate pane is at least 1 mm thick.

4. A composite pane as claimed in any of claims 1 to 3 wherein the synthetic resin protective film is colourless.

5. A composite pane as claimed in any of the preceding claims wherein the synthetic resin protective film is calendered and optically undistorted.

6. A composite pane as claimed in any of the preceding claims wherein the synthetic resin protective film is provided on its surface remote from the adhesive resin layer with a weather-resistant transparent synthetic resin layer.

7. A composite pane as claimed in any of the preceding claims wherein the transparent synthetic resin protective film is provided on its surface remote from the adhesive resin layer, or on the surface of a weather-resistant transparent synthetic resin layer applied thereto, with a scratch-resistant transparent synthetic resin layer.

8. A composite pane as claimed in claim 7 wherein the scratch-resistant layer comprises a scratch-resistant coating of a silicon-containing compound or of polymethyl methacrylate.

9. A composite pane as claimed in any of the preceding claims in which the wear surface of the film applied to the substrate pane has a scratch-resistance which is not lower than that of the substrate pane.

10. A composite pane as claimed in any of the preceding claims wherein the said adhesive resin layer is composed substantially of acrylates.

11. A composite pane as claimed in any of the preceding claims wherein the said adhesive resin layer is free of low molecular weight plasticisers.

12. A composite pane as claimed in any of the preceding claims wherein each of the major surfaces of the substrate pane is provided with a synthetic resin protective film and an intervening trasparent adhesive resin layer as defined in claim 1.

13. A composite pane as claimed in any of the preceding claims in the form of a glazing member.

14. A composite pane as claimed in claim 13 in the form of a glazing member for a vehicle.

15. A method of producing a composite pane as claimed in claim 1 whereby to at least one of the major surfaces of a synthetic resin substrate pane is contacted a transparent synthetic resin protective film provided on the contacting surface with an adhesive resin layer which adheres more firmly to the synthetic resin protective film than to the substrate pane whereby the adhesive resin layer is detachable together with the synthetic resin protective film from the substrate pane.

16. Composite panes as claimed in any of claims 1 to 14 whenever produced by a method as claimed in claim 15.

17. A detachable synthetic resin wear film for use in the production of composite panes as claimed in claim 1 and comprising:

a) at least one transparent synthetic resin protective film;

b) at least one transparent adhesive resin layer firmly adherent to the said transparent synthetic

resin protective film; and

c) if desired, a removable protective coating adherent to the surface of the adhesive resin layer remote from the transparent synthetic resin protective film.

18. A detachable film as claimed in claim 17 wherein the transparent synthetic resin protective film is provided on its surface remote from the adhesive resin layer with a weather-resistant transparent resin layer.

19. A detachable film as claimed in either of claims 17 and 18 wherein the transparent synthetic resin protective film is provided on its surface remote from the adhesive resin layer, or on the surface of a weather-resistant transparent synthetic resin layer applied thereto, with a transparent scratch-resistant synthetic resin layer.

20. A detachable film as claimed in claim 17 comprising:

a) a scratch-resistant silicone synthetic resin layer;

b) a weather-resistant layer of polymethyl methacrylate of 0.2 to 30 microns thickness;

c) a polycarbonate transparent synthetic resin film of 30 to 80 microns thickness;

d) a layer of adhesive resin based on polyethyl hexylacrylate and of 2 to 30 microns thickness; and

e) a water-soluble protective coating of a vinyl ether/maleic acid copolymer.

21. A detachable film as claimed in claim 20 wherein the scratch-resistant silicone synth tic resin layer has a thickness of about 10 microns.

22. Substrate panes whenever provided with a detachable film as claimed in any of claims 17 to 21 from which the said removable protective coating, if present, has been removed.

23. Composite panes as claimed in claim 22 in the form of glazing members.

24. Articles whenever incorporating composite panes as claimed in any of claims 1 to 14, 16, 22 and 23.

25. Articles as claimed in claim 24 in the form of vehicles.

26. Articles as claimed in claim 25 in the form of motor vehicles.

27. Vehicles having composite panes as claimed in any of claims 1 to 14, 16, 22 and 23 fitted approximately parallel to the direction of travel thereof.

28. Composite panes as claimed in claim 1 substantially as herein described.

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